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LETTER TO THE EDITOR

Note on the Theoretical Limit of the Thermoelectric Figure of Merit

THERE have been a number of attempts to arrive at some sort of upper limit to the dimensionless figure of merit [1, 2] ZT of a thermoelectric generator [2–6]. The arguments are based either on irreversible thermodynamics of solid-state theory. Littman and Davidson [2] have shown that, from considerations of entropy production, there is no upper limit to the figure of merit. In this note we will give an alternative derivation of Littman and Davidson's result. We note the very simple fact that the Onsager coefficient L_{ij} cannot be zero in the presence of thermal and electrical gradients. We make use of this condition on L_{ij} in addition to the conditions on the phenomenological coefficients resulting from the positive definite form of the entropy production equation. We will also point out a minor way in which their own derivation can be simplified.

Littman and Davidson show that the entropy production dS/dt when brought into the form

$$\frac{dS}{dt} = \frac{J_2^2}{L_{22}} + \frac{(L_{11}L_{22} - L_{12}L_{21})\,X_1^2}{L_{22}} \geqslant 0 \tag{1}$$

—where J_2 is the heat flow, X_1 the force corresponding to the current density J_1, and L_{ij} are the phenomenological coefficients—yields after some manipulation the inequality,

$$(1 - (L_{21}^2/L_{11}L_{22})) \geqslant 0 \tag{2}$$

The proof that there is no upper limit to Ioffe's figure of merit ZT derives from this inequality. It appears, however, that this inequality can be established directly from the positive semidefinite form of dS/dt when written in terms of the coefficients L_{ij} and the forces X_1, and X_2, (where X_2 is the force corresponding to the heat flow J_2); i.e.,

$$dS/dt = L_{11}X_1^2 + (L_{12} + L_{21})\,X_1X_2 + L_{22}X_2^2 \geqslant 0 \tag{3}$$

Equation (3) leads to the inequalities [7],

$$L_{11} \geqslant 0,\, L_{22} \geqslant 0,\, (L_{11}L_{22} - L_{12}L_{21}) \geqslant 0 \tag{4}$$

or with the Onsager reciprocal relations, $L_{12} = L_{21}$,

$$L_{11}L_{22} \geqslant L_{12}^2 \geqslant 0 \tag{5}$$

which yields immediately equation (2).

It may also be established, directly and simply, that there is no upper limit to the figure of merit by considering the definition of ZT,

$$ZT = \alpha^2\sigma T/K \tag{6}$$

where, α, is the Seebeck coefficient or thermoelectric power, σ, the electrical conductivity, and K, the thermal conductivity. Expressing α, σ, K, in terms of the phenomenological coefficients L_{ij} [8],

$$\begin{aligned} \alpha &= -(L_{12}/L_{11}T) \\ \sigma &= L_{11}/T \\ K &= ((L_{11}L_{22} - L_{12}L_{21})/L_{11}T^2) \end{aligned} \tag{7}$$

and substituting in equation (6), we have,

$$ZT = (L_{12}^2/(L_{11}L_{22} - L_{12}^2)) \tag{8}$$

From equation (4) $(L_{11}L_{22} - L_{12}^2) \geqslant 0$, to which we may add the condition that $L_{12} \neq 0$, because the coefficient L_{12}, after all, expresses the interaction of heatflow and particle flow giving rise to thermoelectricity. Thus, L_{12}^2 is positive definite, and consequently $ZT > 0$, and hence, there is no upper limit to ZT. $ZT = 0$ when $L_{12} = 0$, i.e., there is no thermoelectric effect.

It should be emphasized that the use of the macroscopic solid state properties expressed by α, σ, K, does not in the least imply that the preceding proof is based on solid state theory—the proof clearly hinges on the conditions imposed on the entropy production of the system by the second law of thermodynamics, and places no limitations on the physical properties of the system.

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REFERENCES

[1] A. F. IOFFE, *Semiconductor Thermoelements and Thermoelectric Cooling*, pp. 39. Infosearch, London (1957).
[2] H. LITTMAN and B. DAVIDSON, *J. Appl. Phys.* **32**, 217 (1961).
[3] K. H. SPRING, *Nature, Lond.* **190**, 297 (1961).
[4] PIERRE R. AIGRAIN, Design of Materials for Thermoelectric Power Production, Chapt. 10 in *Thermoelectricity*, (Ed. by PAUL, H. EGLI), pp. 180, Wiley, New York (1960).
[5] F. J. DONOHOE, *Elect. Engng.* **79**, 488 (1960).
[6] E. S. RITTNER, *J. Appl. Phys.* **30**, 702 (1959).
[7] S. R. DE GROOT, *Thermodynamics of Irreversible Processes*, pp. 146, North Holland, Amsterdam (1959).
[8] See reference [6], pp. 143 *et seq.*